



Research Paper

Nickel-doped sodium zirconate catalysts for carbon dioxide storage and hydrogen production through dry methane reforming process



J. Arturo Mendoza-Nieto^{a,*}, Samuel Tehuacanero-Cuapa^b, Jesús Arenas-Alatorre^b, Heriberto Pfeiffer^{a,*}

^a Laboratorio de Fisicoquímica y Reactividad de Superficies (LaFReS), Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Del. Coyoacán, CP 04510 Ciudad de México, Mexico

^b Instituto de Física, Universidad Nacional Autónoma de México, Circuito Exterior s/n, Ciudad Universitaria, Del. Coyoacán, CP 04510, Ciudad de México, Mexico

ARTICLE INFO

Keywords:
CO₂ Chemisorption
Dry CH₄ reforming
NiO catalyst
Sodium zirconate
Syngas

ABSTRACT

NiO-doped sodium zirconate ceramics with different amounts of NiO (between 0 and 10 wt%) were synthetized and characterized by powder XRD, SEM-EDS and N₂ physisorption. Structural and microstructural characteristics of a Na₂ZrO₃ based-ceramic were maintained in all NiO-containing samples. These materials were tested for CO₂ capture (TGA), desorption processes (TPD) and dry CH₄ reforming (DMR, catalytic tests). Initially, samples were dynamically tested for CO₂ chemisorption; these tests showed a slight inhibition for CO₂ capture due to the presence of NiO, which partially blocked Na₂ZrO₃ surface sites where CO₂ can be chemisorbed. Then, NiO-doped samples were carbonated and exposed to a CH₄ flow in order to perform DMR reaction, using carbonate samples as CO₂ source. In all cases, NiO addition resulted in greater production of H₂ than that of pure Na₂ZrO₃. Additionally, a drastic reduction in the reaction temperature was observed, especially for NiO-doped Na₂ZrO₃ containing 10 wt% of NiO. Additionally, regeneration and cyclic behavior showed that it is possible to accomplish consecutive cycles of CO₂ capture-DMR with considerable Na₂ZrO₃ regeneration. On the other hand, cyclability was affected due to a partial NiO reduction after DMR steps. However, if a pre-oxidation step was performed, the catalytic activity and H₂ production were recovered. Hence, it was established that NiO-doped Na₂ZrO₃ materials can be used as bifunctional materials as (i) CO₂ captors and then as (ii) catalytic materials during DMR reaction.

1. Introduction

In recent decades, methane (CH₄) and carbon dioxide (CO₂) emissions have been responsible for climate change and global warming, as both gases are the major contributors to the greenhouse effect [1]. Although the concentration of methane in the atmosphere is much lower than that of CO₂, methane more effectively absorbs infrared radiation, and thus, its contribution to planet warming is significantly higher than that of CO₂ [2]. However, carbon dioxide emissions are the main contaminants and contribute almost 60% for enhancing greenhouse effect each year, whereas methane is the primary component of natural gas and is responsible for 15% of global warming [2–4]. One option for limiting greenhouse effects is to reduce the emission of both gases by converting them into an alternative and cleaner energy source. In this regard, hydrogen (H₂) production through the use of greenhouse gases would be a viable option [6–8]. Among H₂ production processes, the most commonly used are dry methane reforming (DMR) [9–12],

steam methane reforming (SMR) [13,14], sorption-enhanced methane reforming (SEMR) [15–17], water-gas shift reaction (WGSR) [18–20] and ethanol-steam reforming (ESR) [21–23]. These processes all produce synthetic gas (syngas), which is composed of H₂ and carbon oxides (CO or CO₂), depending on the process utilized and reaction conditions. Hence, CO or CO₂ removal is usually a key step to purify H₂. Thus, different technologies have been developed over the past few years to accomplish this necessity [24].

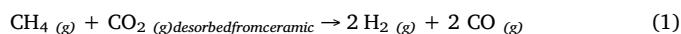
In particular, dry CH₄ reforming does have some disadvantages: (1) the reforming reaction is highly endothermic; (2) high temperatures are required to obtain high conversions, which leads to catalyst deactivation by coke formation; and (3) the H₂ purity from this process is low, and additional operations, such as purification, separation and compression techniques, must be used [25,26]. To achieve this goal, it has been necessary to use two different materials: one acting as a catalyst and a suitable chemical sorbent to eliminate the remaining CO₂ [16,17].

* Corresponding authors.

E-mail addresses: amendozan@comunidad.unam.mx, armeni86@hotmail.com (J.A. Mendoza-Nieto), pfeiffer@iim.unam.mx (H. Pfeiffer).

In this sense, Ni-based catalysts supported over different metal oxides are the most used materials for performing DMR, e.g., Ni/ α -Al₂O₃ [9], Ni/ γ -Al₂O₃ [10] or Ni/Ce_xZr_{1-x}O₂ [11]. On the other hand, CO₂ capture and storage (CCS) [5,27,28] can be achieved using different alkali (Li, Na and K) and earth-alkaline (Be, Mg and Ca) metal-based ceramics as chemical sorbents [29–34], as these CCS materials present high superficial basicity, good sorption-desorption kinetics, thermal stability, high regeneration ability, mechanical strength and selective CO₂ sorption [35].

Recently, sodium zirconate (Na₂ZrO₃) [36] and NiO-CaO composites [37] were synthetized, characterized and tested as possible bi-functional materials, acting as both CO₂ sorbents and then as catalysts for dry CH₄ reforming to obtain a consecutive CO₂ capture and DMR processes. Those results clearly showed that both materials capture CO₂, store it and then supply CO₂ during the DMR process (reaction (1)), thereby producing H₂ at T > 800 °C with Na₂ZrO₃; however, NiO-CaO showed a better catalytic behavior (~500 °C). With these results in mind, the aim of this work was to determine whether NiO addition modifies the CO₂ chemisorption on Na₂ZrO₃ as well as the catalytic activity for H₂ production through the DMR process.



2. Experimental section

2.1. Synthesis and characterization of NiO(x)-Na₂ZrO₃ materials

Sodium zirconate doped with different nickel oxide loadings were synthesized via acetate decomposition. Hereinafter, NiO-doped materials are labeled NiO(x)-Na₂ZrO₃, where x represents the NiO loading used (x = 0.0, 2.5, 5.0, 7.5 and 10 wt%). Sodium acetate (NaC₂H₃O₂, Aldrich), zirconium acetate solution in acetic acid (Zr(C₂H₄O₂)₄, 16.1 wt% Zr, Aldrich) and nickel acetate tetrahydrate (Ni(C₂H₃O₂)₂·4H₂O, 98%, Aldrich) were used as reagents. Due to the likelihood of Na sublimation at temperatures higher than 800 °C, a 15.0 wt% excess of NaC₂H₃O₂ was considered [35,38]. Acetate precursors were dissolved in water and heated at 60 °C until a paste was obtained. A solid product was obtained after two stages of calcination in static air: (1) first, acetate decomposition was carried out via heating at 400 °C for 6 h, then (2) the sodium zirconate crystalline structure was obtained via heating at 900 °C for 12 h.

NiO-containing catalysts were structurally and microstructurally characterized by powder X-ray diffraction (XRD), N₂ adsorption-desorption and analytical scanning electron microscopy (SEM-EDS). XRD patterns were recorded in the 10° ≤ 2θ ≤ 70° range with a goniometer speed of 1° (2θ) min⁻¹, using a Siemens D5000 diffractometer coupled to a cobalt anode (λ = 1.789 Å) X-ray tube. Once the NiO(x)-Na₂ZrO₃ crystalline structures were determined, nitrogen adsorption-desorption isotherms were measured with a Bel-Japan Minisorp II equipment at 77 K using a multipoint technique. Prior to physisorption experiments, samples were degassed at room temperature for 12 h in vacuum (p < 10⁻¹ Pa). The specific surface area (S_{BET}) for each material was calculated with a BET model. CO₂ temperature-programmed desorption (TPD) analyses were performed using a chemisorption analyzer (Belcat, Bel-Japan). Before each analysis, approximately 50 mg of sample was introduced into a quartz cell and pretreated at 850 °C under a He flow (30 mL/min). Each sample was then cooled to 200 °C and saturated with a 60 mL/min flow of CO₂ for 60 min. Afterwards, CO₂-TPD analyses were performed by heating each sample up to 850 °C (heating rate of 2 °C/min) in a He flow, and the data were quantified by a thermal conductivity detector (TCD). Finally, scanning electron microscopy (SEM) coupled to energy dispersive X-ray spectroscopy (EDS) measurements were recorded on a FE-SEM JEOL JSM 7800F electron microscope equipped with an energy dispersive analysis detector Oxford 50 mm² X-Max. The acceleration voltage used was 20 kV and a

backscattered electron detector.

2.2. CO₂ capture and DMR processes

Carbon dioxide capture tests were performed in a Q500HR thermobalance from TA Instruments. NiO(x)-Na₂ZrO₃ samples were heat-treated dynamically from room temperature to 950 °C (heating rate of 3 °C/min). These experiments were performed using ~40 mg of sample and a carbon dioxide (CO₂, Praxair grade 3.0) flow rate of 60 mL/min. After CO₂ capture analysis, NiO(x)-Na₂ZrO₃ catalysts were tested in the dry reforming reaction (DMR) following a previously published procedure [36], using 200 mg of sample in a Bel-Rea catalytic reactor from Bel-Japan. First, NiO-doped samples were carbonated dynamically from 30 to 600 °C (heating rate of 5 °C/min) and then isothermally treated at 600 °C for 0.5 h. Finally, samples were cooled to 200 °C, using a gas mixture composed of 60 vol% CO₂ and 40 vol% N₂ (Praxair grade 4.8). Once samples were carbonated and partially cooled down to 200 °C, the dry methane reforming (DMR) process was performed from 200 to 900 °C (heating rate of 2 °C/min) using 100 mL/min of a gas mixture composed of CH₄ (5 vol%, Praxair grade 5.0) and N₂ balanced. In addition, cyclic experiments of CO₂ capture and subsequent DMR tests were performed with the NiO(10)-Na₂ZrO₃ catalyst. This procedure was performed using the same experimental conditions described above during 5 cycles, adding a sixth cycle, where CO₂ capture and DMR processes were performed after a previous oxidation step under 30 mL of O₂ at 600 °C for 2 h. Reforming gas products were analyzed every 15 °C up to 900 °C (dynamic experiments), or every 8.3 min (isothermal experiments), using a Shimadzu GC-2014 gas chromatograph with a Carbonex-1000 column. After DMR isothermal experiments, some materials were re-characterized by XRD.

3. Results and discussion

3.1. Characterization of NiO(x)-Na₂ZrO₃ materials

Powder XRD patterns for NiO(x)-Na₂ZrO₃ samples (0 ≤ x ≤ 10) are shown in Fig. 1. As expected, Na₂ZrO₃ crystalline planes were observed (PDF file 35-0770) in the pure sample (x = 0.0). X-ray patterns for Na₂ZrO₃ materials doped with different NiO amounts showed the same sodium zirconate crystalline structure. However, Na₂ZrO₃ reflections shifted as a function of nickel oxide content, which indicate some changes in the crystalline unit cell. In addition to Na₂ZrO₃ crystalline variations, these XRD patterns presented three other reflections located at 43.8, 50.9 and 74.6°, in 2θ scale, which increased as a function of the

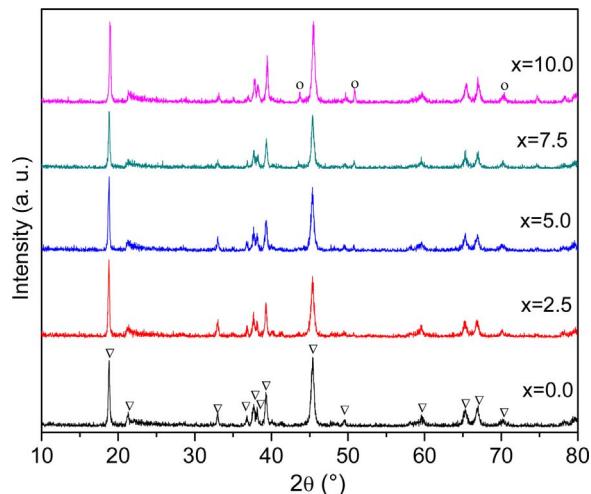


Fig. 1. NiO(x)-Na₂ZrO₃ XRD patterns. Crystalline phases were labeled as; (▽) Na₂ZrO₃ and (○) NiO.

Table 1NiO(x)-Na₂ZrO₃ cell parameters determined from XRD data.

NiO loading	Cell parameters				Cell volume (Å ³)
	a (Å)	b (Å)	c (Å)	β (°)	
0.0	11.104 (2)	9.732 (1)	5.631 (4)	99.60 (2)	600.0 (4)
2.5	11.109 (2)	9.736 (1)	5.633 (4)	99.73 (2)	600.6 (4)
5.0	11.116 (2)	9.741 (1)	5.653 (4)	99.75 (2)	603.4 (4)
7.5	11.116 (2)	9.733 (1)	5.651 (4)	99.87 (2)	602.5 (4)
10.0	11.108 (2)	9.732 (1)	5.603 (4)	99.74 (2)	597.0 (4)

NiO loading used. These reflections are related to NiO formation (PDF file 65-5745). Furthermore, average crystallite size was estimated for NiO(10)-Na₂ZrO₃ sample by using Scherrer correlation and the (0 1 2) reflection located 50.9° in the 2θ scale, obtaining a NiO crystallite size equal to 52.1 nm. In an effort to further analyze the XRD patterns, cell parameters were calculated for NiO(x)-Na₂ZrO₃ samples (Table 1). It was observed that all unit cell parameters depend on nickel loading, presenting NiO-doped samples higher values than pure Na₂ZrO₃, excepting for c parameter which displays the largest variations in NiO (10)-Na₂ZrO₃ sample. The greatest cell expansion was observed with nickel loadings less or equal to 5 wt%. This result indicates that nickel incorporation into crystalline structure was possible at x ≤ 5.0 wt%, which seems to be the solubility limit. In contrast, samples prepared with higher nickel loadings than 5.0 wt% presented a cell contraction, suggesting that part of nickel atoms were incorporated into Na₂ZrO₃ crystalline structure and the rest formed a secondary phase that according to previous XRD patterns corresponds to NiO formation over ceramic surface.

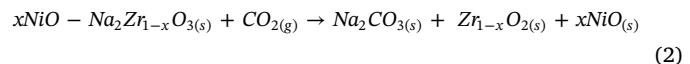
SEM analysis with backscattered electrons and EDS elemental mapping were performed for only two NiO-doped samples: NiO(5)-Na₂ZrO₃ and NiO(10)-Na₂ZrO₃ (Fig. 2). SEM images show two different compounds: a Na₂ZrO₃ phase detected by XRD and a Na₂CO₃ phase formed due to air exposition during analysis. Both NiO-containing samples presented large and dense particles, with particle sizes between 5 and 40 μm with a polyhedral shape (Fig. 2A and D). Additionally, it seems that morphology characteristics did not change as a function of nickel content. Regarding EDS elemental mapping analyses, Fig. 2C and F shows that nickel oxide observed previously by XRD (Fig. 1) is homogeneously distributed over the sodium zirconate surface, allowing a suitable dispersion of metallic particles in both cases.

In a further characterization, a N₂ physisorption technique was applied to determine the textural characteristics of the NiO(x)-Na₂ZrO₃ samples. Nitrogen adsorption-desorption isotherms are shown in Fig. 3. According to IUPAC classification, all materials present type II isotherms related to nonporous materials [39]. In these materials, no significant hysteresis loops were observed. Additionally, specific surface area (S_{BET}) was determined from N₂ adsorption curves using the BET model. The S_{BET} values were between 0.3 and 0.6 m²/g, which are in line with synthesis method used. Additionally, N₂ physisorption results are in good agreement with previous reports for Na₂ZrO₃ materials [35,40,41]. Hence, nickel addition does not significantly modify Na₂ZrO₃ textural properties.

3.2. Carbon dioxide capture, storage and desorption

Once the NiO(x)-Na₂ZrO₃ samples were characterized; they were thermally treated from 30 to 950 °C under CO₂ flow into a thermobalance. Thermograms are shown in Fig. 4. All profiles exhibit a similar bimodal distribution as a function of temperature. First, an initial weight increase is observed between 100 and 400 °C, which is associated with CO₂ a chemisorption process over the Na₂ZrO₃ particle surfaces, according to previous reports [41,42]. In this step, a thin Na₂CO₃-ZrO₂ external shell is formed only over Na₂ZrO₃ particles (reaction (2)). It should be noted that all nickel-containing samples

presented a lower superficial carbonation than that observed in the Na₂ZrO₃ case. This carbonation decrement must be totally related to nickel oxide formation which was not incorporated into the Na₂ZrO₃ structure (see XRD results) but instead on the Na₂ZrO₃ particle surface, reducing CO₂ sorption sites.



All thermograms show a second weight increase at temperatures above 450 °C. This distribution is at least six or seven times greater than the superficial process discussed above and represents the highest amount of CO₂ captured (between 16.1–18.7 wt%). Weight increases in this temperature range are associated with activation of different diffusion processes [43], allowing bulk CO₂ chemisorption. This second CO₂ capture process was not affected by the nickel presence superficial, as NiO, or structurally into the Na₂ZrO₃ structure. In fact, curve slopes observed in this section did not vary significantly. Finally, in all NiO-containing materials, CO₂ desorption phenomena which registered in other Na₂ZrO₃ materials at approximately 800–850 °C [41,42], were not observed until 950 °C even in a pristine Na₂ZrO₃ sample. This result may be related to the low S_{BET} obtained in synthetized samples. In this case, a Na₂ZrO₃ ceramic synthetized without NiO addition demonstrated the best thermal behavior among all samples tested in the capture experiments and resulted in the highest amount of CO₂ chemisorbed (18.7 wt%) at 950 °C. Furthermore, Fig. 4 shows that an increase in the NiO composition causes a CO₂ chemisorption decrease of 1–3 wt% over the entire temperature range. Despite this decrease, NiO (x)-sodium zirconate materials chemisorbed between 16.1 and 17.7 wt % of CO₂ at 950 °C. Theoretical maximum capture values were calculated as a function of NiO content considering reaction (2), 23.8 wt% for x = 0.0 and 23.3 wt% for x = 10.0. Then, efficiencies were calculated as a ratio between experimental and theoretical values, obtaining values between 68–75% as NiO content (x) increases from 2.5 to 10.0%, while pure Na₂ZrO₃ (x = 0.0) presented an efficiency of 79%. As it can be seen, nickel addition produces a maximum efficiency reduction of 11%; this reduction may not be so important if nickel oxide contributes catalytically during DMR (see next Section 3.3).

CO₂-TPD experiments were performed with different NiO(x)-Na₂ZrO₃ samples in order to determine the effect of NiO addition on CO₂ desorption abilities (Fig. 5). Regardless of the NiO content used, TPD profiles exhibit two desorption steps. The first one is located between 200 and 260 °C with a maximum approximately 225 °C, which is ascribed to a superficial chemisorption on Na₂ZrO₃ type materials (weakly bound CO₂). This desorption step shows almost the same thermal behavior in all samples. Meanwhile, the second signal shows the highest CO₂ desorption (550 and 850 °C), which can be attributed to a stronger bound CO₂ sorption over ceramic particles. For this step, it was observed that nickel addition induces a progressive reduction into CO₂ desorption temperature. Thus, NiO(10)-Na₂ZrO₃ sample showed CO₂ desorption which began at 550 °C with a maximum located at 765 °C, whereas pure Na₂ZrO₃ (x = 0.0) showed the highest temperature values (CO₂ desorption began at 650 °C with a maximum at 800 °C) among all samples tested. After TGA and TPD results, it was established that all NiO(x)-Na₂ZrO₃ materials, containing nickel oxide or not, are able not only to capture CO₂ but also able to store and desorb it over wide temperature range; therefore, NiO(x)-Na₂ZrO₃ materials are proposed as potential carbonated materials for other catalytic applications such as DMR process (reaction (1)).

3.3. Dry methane reforming (DMR)

After CO₂ capture and desorption analyses, a two-step process was performed to produce syngas (H₂ + CO). This process consisted of CO₂ capture at 600 °C on NiO(x)-Na₂ZrO₃ materials followed by a catalytic conversion between CH₄ and the previously captured CO₂. Notably, the carbonation process was performed at 600 °C, in line with previously

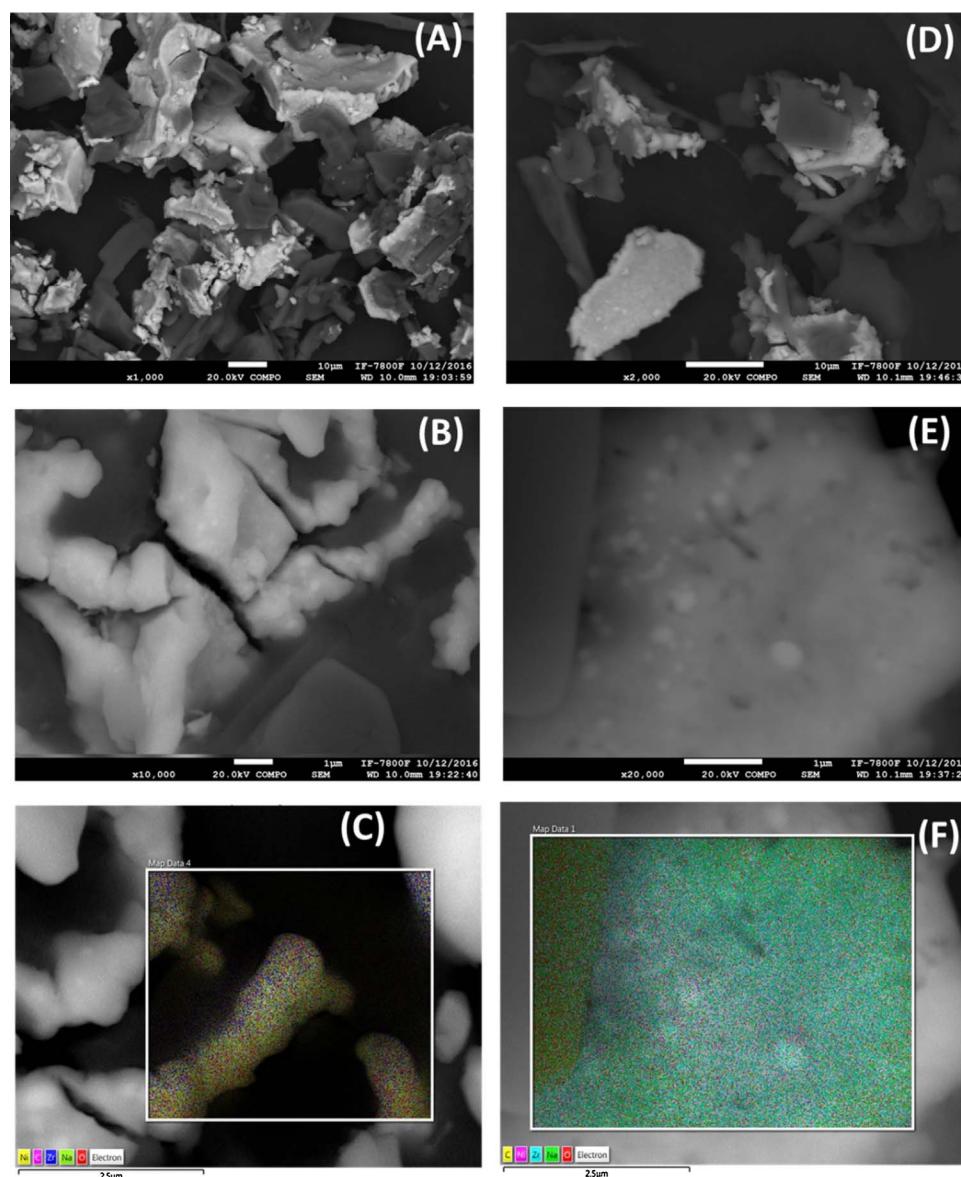


Fig. 2. SEM images and EDS elemental mapping for NiO(5)-Na₂ZrO₃ (A–B and C) and NiO(10)-Na₂ZrO₃ (D–E and F) materials.

published methods [36], where it was posed that at this temperature, Na₂ZrO₃ presents the highest CO₂ chemisorption. Fig. 6 shows reactants (CH₄ and CO₂) and products (H₂ and CO) evolution as a function of temperature for the Na₂ZrO₃ and NiO(10)-Na₂ZrO₃ samples. When the Na₂ZrO₃ sample was tested, H₂ production was detected from 785 °C, indicating that CH₄ reforming process occurs at relatively high temperatures. In fact, at higher temperatures, hydrogen formation became more evident, reached a 10% efficiency at 900 °C, and fit well with the CH₄ reduction content (Fig. 6A). It seems that hydrogen production is mainly generated at high temperatures through a partial CH₄ oxidation process, because CO₂ desorption from Na₂ZrO₃ sample occurred at a lower temperature range (600–850 °C), which indicated that desorbed CO₂ did not react with methane-producing syngas. This catalytic behavior is in good agreement with previous results [36], where similar H₂ amounts were obtained between 800 and 900 °C with a Na₂ZrO₃ material prepared via solid state method. Additionally, it can be observed that the H₂/CO ratio is lower than 1.0 from 700 to 860 °C, indicating that CO formation was greater than H₂ production, until the temperature reached T > 870 °C, where H₂/CO ratio was higher than 1.0. According to the literature [25], H₂/CO < 1.0 can be rationalized by the fact that the reverse water-gas shift reaction (where H₂ formed reacts with CO₂), occurred simultaneously with the DMR reaction.

In contrast, catalytic evolution for the carbonated NiO(10)-Na₂ZrO₃ sample showed a totally different behavior for the DMR reaction (Fig. 6B). H₂ production shows four maxima at 550, 650, 835 and 900 °C, reaching 11.3, 26.1, 18.6 and 20.9% efficiencies, respectively. At 550 and 650 °C, H₂ production is in good agreement to CO₂ desorption, and confirms the DMR reaction. Here, the CH₄ concentration decreased at those temperatures, while H₂ and CO increased. At higher temperatures (T > 835 °C), hydrogen and carbon monoxide production are observed, with a corresponding CH₄ reduction. However, CO₂ desorption was not detected, showing that at high temperatures, H₂ formation was produced due to partial CH₄ oxidation, as CO₂ seems to be absent in gas mixture. In contrast to the H₂/CO ratios obtained for the pure Na₂ZrO₃ sample, in all temperature ranges evaluated with the NiO(10)/Na₂ZrO₃ catalyst, it was observed that H₂/CO ratios were between 1.01 and 1.92, indicating that H₂ production is always higher than CO formation. Additionally, at some temperatures (600–635 and 665–720 °C), the H₂/CO ratio was almost equal to 1.0, suggesting that reverse water gas shift reaction was not possible [25]. The above results clearly show that using Na₂ZrO₃ with NiO drastically enhances syngas production in comparison to the use of pure Na₂ZrO₃ (Fig. 6A).

To understand the NiO effect on hydrogen production, a series of NiO(x)-Na₂ZrO₃ materials doped with different NiO loads

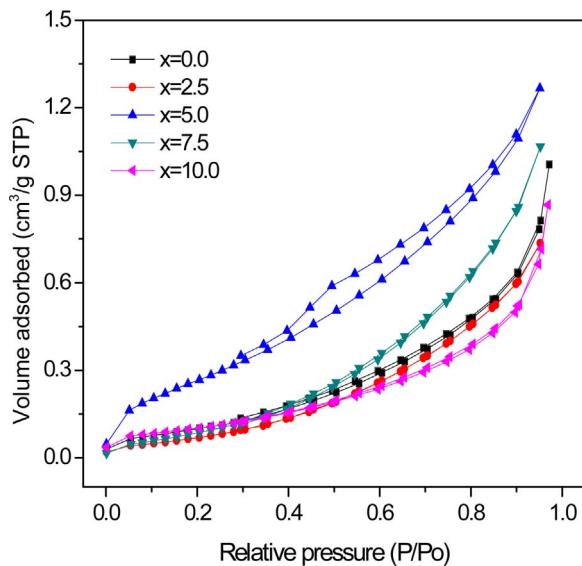


Fig. 3. N₂ adsorption-desorption isotherms at 77 K for NiO(x)-Na₂ZrO₃ materials prepared with different NiO loadings.

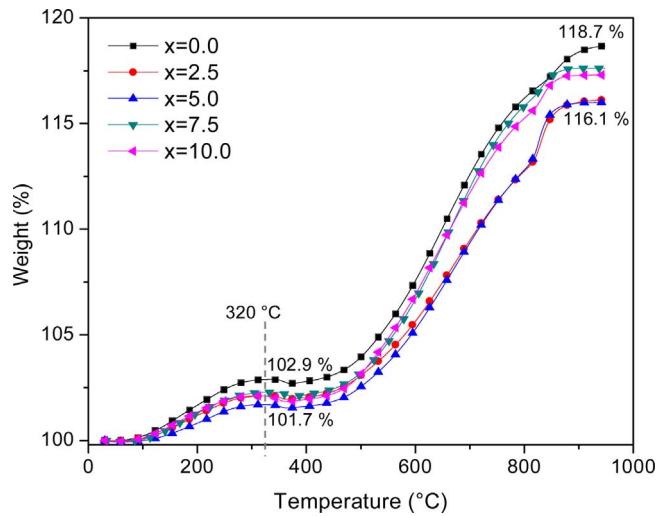


Fig. 4. Thermogravimetric analyses for NiO(x)-Na₂ZrO₃ samples tested dynamically from 30 to 900 °C in a saturated CO₂ atmosphere (60 mL/min).

($2.5 \leq x \leq 10$) were tested in DMR reactions. Fig. 7 shows the thermal evolution for H₂ production using these NiO(x)-Na₂ZrO₃ catalysts. As can be seen, hydrogen formation and production temperature are a function of nickel content. In general, Ni addition not only causes an increase in H₂ formed, but also does so at lower temperatures. NiO(x)-Na₂ZrO₃ profiles exhibit some differences in comparison to pure Na₂ZrO₃ ceramic, as was described above. When sodium zirconate was doped with 2.5, 5.0 and 7.5 wt% of NiO, a bimodal profile was observed and is shown in Fig. 7. In addition to the temperature range for CH₄ reduction observed in pure Na₂ZrO₃ between 850 and 900 °C; another signal for H₂ production was detected in a lower temperature range (750–850 °C), increasing from 9.2% in the NiO(2.5)-Na₂ZrO₃ sample to 15.0% in the NiO(7.5)-Na₂ZrO₃ material. Not only was a larger amount of H₂ obtained as the Ni content increased but also the temperature decreased from 850 to 816 °C, consistent with the behavior observed during TPD analyses (see Fig. 5). Finally, when the highest amount of NiO ($x = 10.0$ wt%) was added to Na₂ZrO₃, the best catalytic behavior was observed in terms of a significant increase in hydrogen formation and a decrease in temperature. Therefore, the catalytic behavior observed at $T < 800$ °C can be due to DMR occurred over the NiO species

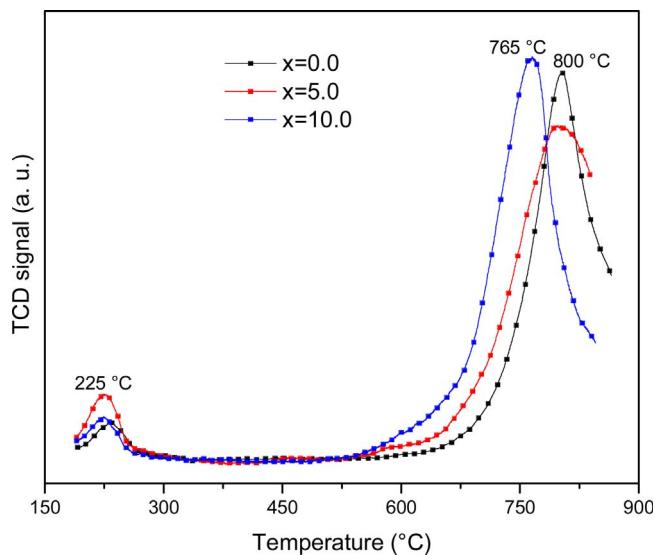


Fig. 5. CO₂-TPD desorption profiles for carbonated NiO(x)-Na₂ZrO₃ samples heat treated from 200 to 850 °C in a He flow.

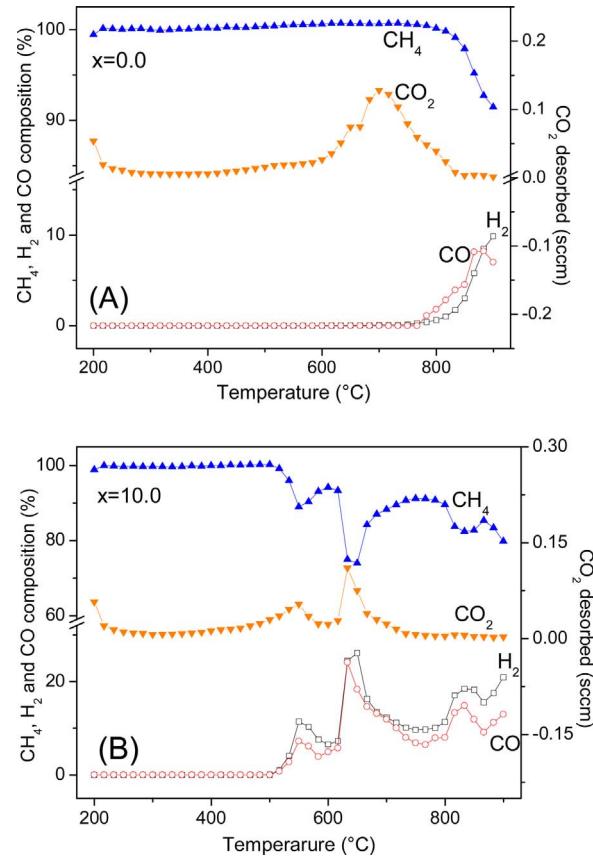


Fig. 6. Dynamic evolution (200–900 °C) for reactants (CO₂ and CH₄) and products (CO and H₂) obtained after CO₂ capture and CH₄ reforming processes using NiO(x)-Na₂ZrO₃ samples with different NiO compositions: (A) $x = 0.0$ and (B) $x = 10.0$. CO₂ average quantification is not possible as it was desorbed from the ceramics, thus it is only reported in sccm units.

located at the surface of sodium zirconate catalysts. A similar result had been previously observed for a DMR reaction using NiO-CaO composites. In that case, H₂ production occurred between 500 and 700 °C and it was ascribed to the NiO presence at the ceramic surface [37].

To analyze possible cyclability for NiO(10)-Na₂ZrO₃ sample during CO₂ capture and subsequent DMR, six cycles were performed with the

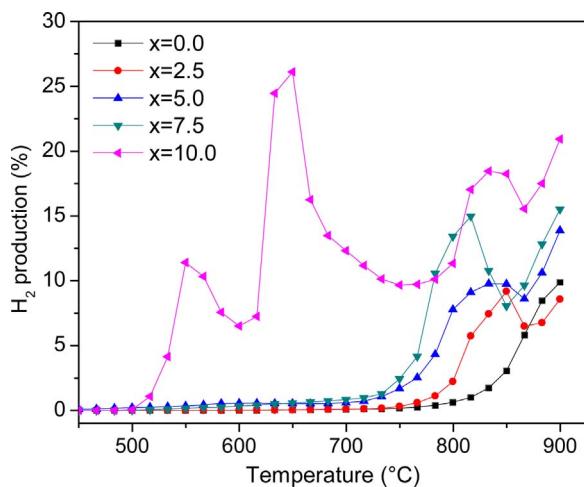


Fig. 7. Hydrogen formation obtained during dry methane reforming process, using NiO (x)-Na₂ZrO₃ catalysts with different Ni loadings.

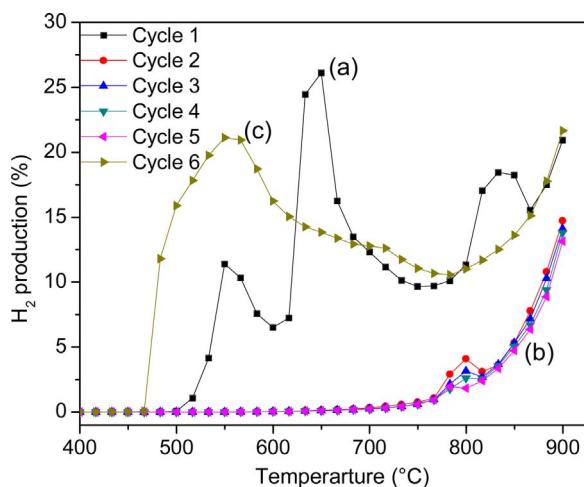


Fig. 8. Cyclic CO₂ carbonation-DMR tests, using a pristine NiO(10)-Na₂ZrO₃ material in cycle 1 (a), a reduced Ni(10)-Na₂ZrO₃ sample in cycles 2–5 (b) and a re-oxidized NiO(10)-Na₂ZrO₃ material in cycle 6 (c).

same physicochemical conditions previously described in the experimental section. Fig. 8 shows hydrogen formation as a function of temperature in each cycle. The catalytic performance between 800 and 900 °C did not change during cyclic tests. In contrast, catalytic behavior at T < 800 °C depends strongly on the number of cycles performed. H₂ production decreases drastically between the cycles 2 and 5, with H₂ formation lower than 5% in these cycles at approximately 800 °C. The main reason for this decrement may be due to NiO reduction to metallic nickel during DMR steps. To test whether the nickel oxidation state was responsible for this phenomenon, a sixth cycle was performed with a previous oxidation stage (see experimental section). The result showed that hydrogen production increases drastically between the fifth and sixth cycles, reaches the highest H₂ production (21.1%) at 550 °C and maintains the same catalytic behavior at T > 850 °C (Fig. 8). In fact, the temperature range for H₂ production improved as well. It means that DMR and partial oxidation processes were enhanced after catalyst oxidation stage, proving that the catalytic process highly depends on the oxidation state of nickel.

Finally, after CO₂ capture and the subsequent CH₄ reforming process, it should be determined whether sodium zirconate doped with 10 wt% of NiO could be regenerated through these processes as well as through the NiO reduction process. Thus, different sample products were analyzed by X-ray diffraction (XRD), where the pristine NiO(10)-

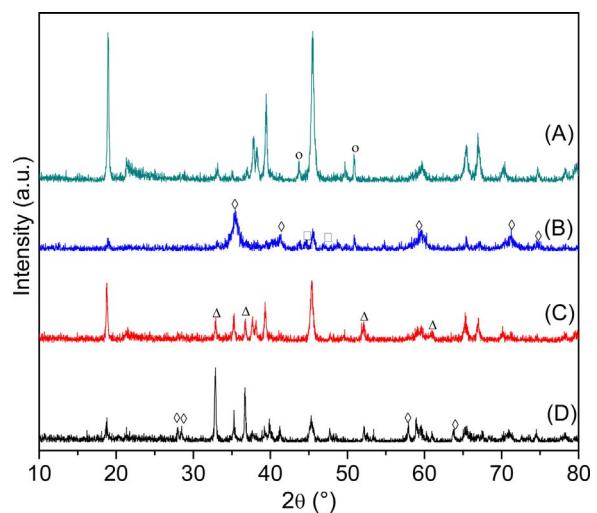


Fig. 9. XRD patterns for (A) original NiO(10)-Na₂ZrO₃, (B) dynamically carbonated-NiO(10)-Na₂ZrO₃ sample, (C) NiO(10)-Na₂ZrO₃ obtained after one cycle and (D) after six cycles of CO₂ capture-DMR. The secondary crystalline phases were labeled as: (○) NiO, (□) Na₂CO₃, (◊) tetragonal and (Δ) monoclinic ZrO₂.

Na₂ZrO₃ was included for comparison purposes (Fig. 9). When the NiO (10)-Na₂ZrO₃ sample was carbonated at 600 °C, the XRD pattern changed drastically and showed Na₂CO₃ (JCPDS card 37-0451) and ZrO₂ (JCPDS card 37-0451) formations, as could be expected. Differences in peak intensities between ZrO₂ and Na₂CO₃ phases are due to a gap in corresponding Zr and Na diffraction scattering coefficients. Finally, X-ray diffraction patterns for products obtained after one or six CO₂ capture-DMR cycles showed Na₂ZrO₃ as the main crystalline phase, as well as two ZrO₂ phases (tetragonal and monoclinic), as minor secondary phases. The above result clearly shows that a partial ceramic regeneration is produced after the CH₄ reforming reaction. However, the Na₂ZrO₃ regeneration degree depends on the number of cycles performed. On the other hand, two ZrO₂ crystalline phases were detected, indicating that part of the Na content was lost during cycle experiments, perhaps through Na sublimation during thermal Na₂CO₃ decomposition [44]. In the ZrO₂ tetragonal case, it may be produced by a Na-doped ZrO₂ structure [45]. Sodium sublimation may be controlled by reducing the final temperature reached in catalytic tests. Finally, it should be mentioned that metallic nickel could not be detected by XRD. Perhaps the amount or dispersion of metallic nickel did not allow its detection due to XRD detection limits.

4. Conclusions

In the present work, sodium zirconate materials doped with different nickel loads were synthesized, characterized and tested in two consecutive processes: (1) carbon dioxide capture and (2) DMR. According to characterization results (XRD, SEM-EDS and N₂ physisorption), it was possible to obtain NiO-doped Na₂ZrO₃ ceramics and maintain the main structure and characteristics of the sodium-containing ceramic. However, when the added NiO amount was greater than or equal to 7.5 wt%, it was not totally incorporated into the Na₂ZrO₃ crystal phase, forming NiO on the ceramic surface. After structural and microstructural characterization, the TG analysis showed that all Ni-containing materials can be used as CO₂ captors over a wide temperature range (200–900 °C), although the NiO presence slightly decreased the CO₂ chemisorption ability by 2–3 wt%, in comparison with Na₂ZrO₃. On the other hand, CO₂-TPD results showed that NiO addition promotes a significant decrease in Na₂ZrO₃ abilities for CO₂ desorption. In particular, a decrement of almost 100 °C was observed for the Na₂ZrO₃ sample prepared with 10 wt% of NiO.

All NiO(x)-Na₂ZrO₃ materials synthesized were carbonated and

subsequently used as a CO₂ source during DMR in order to produce syngas (CO + H₂). Catalytic results showed that all Ni-containing materials produced hydrogen and regenerate after the catalytic process. It was observed that increasing NiO resulted in a lowering of the catalytic temperature as well as a dramatic increase in the H₂ formed. Thus, the best catalytic behavior was obtained with Na₂ZrO₃ ceramic doped with 10 wt% of NiO. This sample produced H₂ over a wide temperature range (500–900 °C), optimal conditions occurred at 650 °C, where the highest H₂ formation was obtained, 26.1%. In fact, two different reactions generated syngas production: (i) DMR at T < 800 °C and (ii) partial CH₄ oxidation at T > 800 °C. Moreover, it was noticed that NiO (10)-doped material cyclability was reduced by means of NiO reduction to metallic Ni. Finally, it was found that performing an oxidation step after the DMR process promotes a re-oxidation of Ni, which allows it to maintain the H₂ production.

Acknowledgments

This work was financially supported by SENER-CONACYT (251801) and PAPIIT-UNAM (IN-101916) projects. J. A. Mendoza-Nieto thanks DGAPA-UNAM for financial support. Authors thank to A. Tejeda for technical help.

References

- [1] S.J. Chapman, M. Thurlow, The influence of climate on CO₂ and CH₄ emissions from organic soils, *Agric. For. Meteorol.* 79 (1996) 205–217, [http://dx.doi.org/10.1016/0168-1923\(95\)02283-X](http://dx.doi.org/10.1016/0168-1923(95)02283-X).
- [2] K.B. Bartlett, R.C. Harris, Review and assessment of methane emissions from wetlands, *Chemosphere* 26 (1993) 261–320, [http://dx.doi.org/10.1016/0045-6535\(93\)90427-7](http://dx.doi.org/10.1016/0045-6535(93)90427-7).
- [3] S. Ma'mun, H.F. Svendsen, K.A. Hoff, O. Juliussen, Selection of new absorbents for carbon dioxide capture, *Energy Convers. Manage.* 48 (2007) 251–258, <http://dx.doi.org/10.1016/j.enconman.2006.04.007>.
- [4] D.T. Allen, V.M. Torres, J. Thomas, D.W. Sullivan, M. Harrison, A. Hendler, S.C. Herndon, C.E. Kolb, M.P. Fraser, A.D. Hill, B.K. Lamb, J. Miskimins, R.F. Sawyer, J.H. Seinfeld, Measurements of methane emissions at natural gas production sites in the United States, *Proc. Natl. Acad. Sci.* 110 (2013) 17768–17773, <http://dx.doi.org/10.1073/pnas.1304880110>.
- [5] S. Nanda, S.N. Reddy, S.K. Mitra, J.A. Kozinski, The progressive routes for carbon capture and sequestration, *Energy Sci. Eng.* 4 (2016) 99–122, <http://dx.doi.org/10.1002/ese3.117>.
- [6] M.C.J. Bradford, M.A. Vannice, CO₂ reforming of CH₄, *Catal. Rev.* 41 (1999) 1–42, <http://dx.doi.org/10.1081/CR-100101948>.
- [7] J.D. Holladay, J. Hu, D.L. King, Y. Wang, An overview of hydrogen production technologies, *Catal. Today* 139 (2009) 244–260, <http://dx.doi.org/10.1016/j.cattod.2008.08.039>.
- [8] M. Momirlan, T. Veziroğlu, Recent directions of world hydrogen production, *Renew. Sustain. Energy Rev.* 3 (1999) 219–231, [http://dx.doi.org/10.1016/S1364-0321\(98\)00017-3](http://dx.doi.org/10.1016/S1364-0321(98)00017-3).
- [9] Y. Cui, H. Zhang, H. Xu, W. Li, Kinetic study of the catalytic reforming of CH₄ with CO₂ to syngas over Ni/α-Al₂O₃ catalyst: the effect of temperature on the reforming mechanism, *Appl. Catal. A Gen.* 318 (2007) 79–88, <http://dx.doi.org/10.1016/j.apcata.2006.10.044>.
- [10] C.A.M. Abreu, D.A. Santos, J.A. Pacífico, N.M. Lima Filho, Kinetic evaluation of methane-carbon dioxide reforming process based on the reaction steps, *Ind. Eng. Chem. Res.* 47 (2008) 4617–4622, <http://dx.doi.org/10.1021/ie071546y>.
- [11] A. Wolfbeisser, O. Sophiphun, J. Bernardi, J. Wittayakun, K. Föttinger, G. Rupprecht, Methane dry reforming over ceria-zirconia supported Ni catalysts, *Catal. Today* 277 (2016) 234–245, <http://dx.doi.org/10.1016/j.cattod.2016.04.025>.
- [12] B. Djebbari, V.M. Gonzalez-Delacruz, D. Halliche, K. Bachari, A. Saadi, A. Caballero, J.P. Holgado, O. Cherifi, Promoting effect of Ce and Mg cations in Ni/Al catalysts prepared from hydrotalcites for the dry reforming of methane, *React. Kinet. Mech. Catal.* 111 (2014) 259–275, <http://dx.doi.org/10.1007/s11144-013-0646-2>.
- [13] A.F. Lucrédio, E.M. Assaf, Cobalt catalysts prepared from hydrotalcite precursors and tested in methane steam reforming, *J. Power Sources* 159 (2006) 667–672, <http://dx.doi.org/10.1016/j.jpowsour.2005.10.108>.
- [14] A. Sauvet, J.T.S. Irvine, Catalytic activity for steam methane reforming and physical characterisation of La_{1-x}Sr_xCr_{1-y}Ni_yO_{3-δ}, *Solid State Ionics* 167 (2004) 1–8, <http://dx.doi.org/10.1016/j.ssi.2003.11.021>.
- [15] M.H. Halabi, J.M. De Croon, J. Van Der Schaaf, P.D. Cobden, J.C. Schouten, Reactor modeling of sorption-enhanced autothermal reforming of methane. Part I: performance study of hydrotalcite and lithium zirconate-based processes, *Chem. Eng. J.* 168 (2011) 872–882, <http://dx.doi.org/10.1016/j.cej.2011.02.015>.
- [16] M.H. Halabi, M.H.J.M. de Croon, J. van der Schaaf, P.D. Cobden, J.C. Schouten, Reactor modeling of sorption-enhanced autothermal reforming of methane. Part II: effect of operational parameters, *Chem. Eng. J.* 168 (2011) 883–888, <http://dx.doi.org/10.1016/j.cej.2011.02.016>.
- [17] J.R. Hufton, S. Mayorga, S. Sircar, Sorption-enhanced reaction process for hydrogen production, *AIChE J.* 45 (1999) 248–256, <http://dx.doi.org/10.1002/aic.690450205>.
- [18] Y. Li, Q. Fu, M. Flytzani-Stephanopoulos, Low-temperature water-gas shift reaction over Cu and Ni-loaded cerium oxide catalysts, *Appl. Catal. B Environ.* 27 (2000) 179–191, [http://dx.doi.org/10.1016/S0926-3373\(00\)00147-8](http://dx.doi.org/10.1016/S0926-3373(00)00147-8).
- [19] Q. Fu, W. Deng, H. Saltsburg, M. Flytzani-Stephanopoulos, Activity and stability of low-content gold–cerium oxide catalysts for the water–gas shift reaction, *Appl. Catal. B Environ.* 56 (2005) 57–68, <http://dx.doi.org/10.1016/j.apcatb.2004.07.015>.
- [20] A. Sandoval, A. Gómez-Cortés, R. Zanella, G. Díaz, J.M. Saniger, Gold nanoparticles: support effects for the WGS reaction, *J. Mol. Catal. A Chem.* 278 (2007) 200–208, <http://dx.doi.org/10.1016/j.molcata.2007.09.014>.
- [21] A. López Ortiz, M.A. Escobedo Bretado, J. Salinas Gutiérrez, M. Meléndez Zaragoza, R.H. Lara Castro, V. Collins Martínez, Na₂ZrO₃ stability under reforming/re-generation cycles during the steam reforming of ethanol with CO₂ absorption, *Int. J. Hydrogen Energy* 40 (2015) 17192–17199, <http://dx.doi.org/10.1016/j.ijhydene.2015.08.020>.
- [22] D.Y. Aceves Olivias, M.R. Baray Guerrero, M.A. Escobedo Bretado, M. Marques da Silva Paula, J. Salinas Gutiérrez, V. Guzmán Velderrain, A. López Ortiz, V. Collins Martínez, Enhanced ethanol steam reforming by CO₂ absorption using CaO, CaO*MgO or Na₂ZrO₃, *Int. J. Hydrogen Energy* 39 (2014) 16595–16607, <http://dx.doi.org/10.1016/j.ijhydene.2014.04.156>.
- [23] K. Essaki, T. Muramatsu, M. Kato, Effect of equilibrium-shift in the case of using lithium silicate pellets in ethanol steam reforming, *Int. J. Hydrogen Energy* 33 (2008) 6612–6618, <http://dx.doi.org/10.1016/j.ijhydene.2008.08.025>.
- [24] S.D. Kenarsari, D. Yang, G. Jiang, S. Zhang, J. Wang, A.G. Russell, Q. Wei, M. Fan, Review of recent advances in carbon dioxide separation and capture, *RSC Adv.* 3 (2013) 22739–22773, <http://dx.doi.org/10.1039/c3ra43965h>.
- [25] J. Montoya, E. Romero-Pascual, C. Gimón, P. Del Ángel, A. Monzón, Methane reforming with CO₂ over Ni/ZrO₂–CeO₂ catalysts prepared by sol–gel, *Catal. Today* 63 (2000) 71–85, [http://dx.doi.org/10.1016/S0920-5861\(00\)00447-8](http://dx.doi.org/10.1016/S0920-5861(00)00447-8).
- [26] J.-M. Lavoie, Review on dry reforming of methane, a potentially more environmentally-friendly approach to the increasing natural gas exploitation, *Front. Chem.* 2 (2014), <http://dx.doi.org/10.3389/fchem.2014.00081>.
- [27] T.F. Wall, Combustion processes for carbon capture, *Proc. Combust. Inst.* 31 (2007) 31–47, <http://dx.doi.org/10.1016/j.proci.2006.08.123>.
- [28] J. Gibbins, H. Chalmers, Carbon capture and storage, *Energy Policy* 36 (2008) 4317–4322, <http://dx.doi.org/10.1016/j.enpol.2008.09.058>.
- [29] M. Kato, K. Essaki, K. Nakagawa, Y. Suyama, K. Terasaka, CO₂ absorption properties of lithium ferrite for application as a high-temperature CO₂ absorbent, *J. Ceram. Soc. Japan* 113 (2005) 684–686, <http://dx.doi.org/10.2109/jcersj.113.684>.
- [30] A. Samanta, A. Zhao, G.K.H. Shimizu, P. Sarkar, R. Gupta, Post-combustion CO₂ capture using solid sorbents: a review, *Ind. Eng. Chem. Res.* 51 (2012) 1438–1463, <http://dx.doi.org/10.1021/ie200686q>.
- [31] M.J. Moreno-Ramírez, I.C. Romero-Ibarra, J. Ortiz-Landeros, H. Pfeiffer, Alkaline and alkaline-earth ceramic oxides for CO₂ capture, separation and subsequent catalytic chemical conversion, CO₂ Sequestration Valorization, InTech, 2014, <http://dx.doi.org/10.5772/57444>.
- [32] T. Nakagawa, K. Ohashi, A novel method of CO₂ capture from high temperature gases, *J. Electrochem. Soc.* 145 (1998) 1344–1346, <http://dx.doi.org/10.1149/1.1838462>.
- [33] J. Wang, L. Huang, R. Yang, Z. Zhang, J. Wu, Y. Gao, Q. Wang, D. O'Hare, Z. Zhong, Recent advances in solid sorbents for CO₂ capture and new development trends, *Energy Environ. Sci.* 7 (2014) 3478–3518, <http://dx.doi.org/10.1039/C4EE01647E>.
- [34] O. Ovalle-Encinia, J.A. Mendoza-Nieto, J. Ortiz-Landeros, H. Pfeiffer, Ce_{0.8}Sm_{0.15}Sr_{0.05}O₂ as possible oxidation catalyst and assessment of the CaO addition in the coupled CO Oxidation–CO₂ capture process, *Ind. Eng. Chem. Res.* 56 (2017) 6124–6130, <http://dx.doi.org/10.1021/acs.iecr.6b04872>.
- [35] J.A. Mendoza-Nieto, H. Pfeiffer, Thermogravimetric study of sequential carbonation and decarbonation processes over Na₂ZrO₃ at low temperatures (30–80 °C): relative humidity effect, *RSC Adv.* 6 (2016) 66579–66588, <http://dx.doi.org/10.1039/C6RA12533F>.
- [36] J.A. Mendoza-Nieto, E. Vera, H. Pfeiffer, Methane reforming process by means of a carbonated-Na₂ZrO₃ catalyst, *Chem. Lett.* 45 (2016) 3–6, <http://dx.doi.org/10.1246/cl.160136>.
- [37] A. Cruz-Hernández, J.A. Mendoza-Nieto, H. Pfeiffer, NiO–CaO materials as promising catalysts for hydrogen production through carbon dioxide capture and subsequent dry methane reforming, *J. Energy Chem.* (2017), <http://dx.doi.org/10.1016/j.jechem.2017.07.002>.
- [38] V.L. Mejía-Trejo, E. Fregoso-Israel, H. Pfeiffer, Textural, structural, and CO₂ chemisorption effects produced on the lithium orthosilicate by its doping with sodium (Li_{4-x}Na_xSiO₄), *Chem. Mater.* 20 (2008) 7171–7176, <http://dx.doi.org/10.1021/cm802132t>.
- [39] S. Lowell, J.E. Shields, M.A. Thomas, M. Thommes, Characterization of Porous Solids and Powders: Surface Area, Pore Size and Density, Springer, Netherlands, Dordrecht, 2004, <http://dx.doi.org/10.1007/978-1-4020-2303-3>.
- [40] G.G. Santillán-Reyes, H. Pfeiffer, Analysis of the CO₂ capture in sodium zirconate (Na₂ZrO₃). Effect of the water vapor addition, *Int. J. Greenh. Gas Control* 5 (2011) 1624–1629, <http://dx.doi.org/10.1016/j.ijggc.2011.09.009>.
- [41] H. Pfeiffer, C. Vázquez, V.H. Lara, P. Bosch, Thermal behavior and CO₂ absorption of Li_{2-x}Na_xZrO₃ solid solutions, *Chem. Mater.* 19 (2007) 922–926, <http://dx.doi.org/10.1021/cm0623965>.
- [42] I. Alcérreca-Corte, E. Fregoso-Israel, H. Pfeiffer, CO₂ absorption on Na₂ZrO₃: a

- kinetic analysis of the chemisorption and diffusion processes, *J. Phys. Chem. C* 112 (2008) 6520–6525, <http://dx.doi.org/10.1021/jp710475g>.
- [43] J. Ortiz-Landeros, T.L. Ávalos-Rendón, C. Gómez-Yáñez, H. Pfeiffer, Analysis and perspectives concerning CO₂ chemisorption on lithium ceramics using thermal analysis, *J. Therm. Anal. Calorim.* 108 (2012) 647–655, <http://dx.doi.org/10.1007/s10973-011-2063-y>.
- [44] J.-W. Kim, H.-G. Lee, Thermal and carbothermic decomposition of Na₂CO₃ and Li₂CO₃, *Metall. Mater. Trans. B* 32 (2001) 17–24, <http://dx.doi.org/10.1007/s11663-001-0003-0>.
- [45] L. Martínez-dlCruz, H. Pfeiffer, Cyclic CO₂ chemisorption–desorption behavior of Na₂ZrO₃: structural, microstructural and kinetic variations produced as a function of temperature, *J. Solid State Chem.* 204 (2013) 298–304, <http://dx.doi.org/10.1016/j.jssc.2013.06.014>.